

蕨类植物里白中一个新的对映 - 贝壳杉烷型二萜化合物

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摘要: 从蕨类植物里白 (*Hicriopteris glauca*) 的丙酮提取物中分离得到 10 个化合物, 包括一个新的对映 - 贝壳杉烷型二萜化合物, 其化学结构通过各种波谱学方法鉴定为 *ent*-2- -hydroxyl-16-ene-kauran-19-oic acid (1)。

关键词: 蕨类植物; 里白; 对映 - 贝壳杉烷二萜; *ent*-2- -hydroxyl-16-ene-kauran-19-oic acid

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A New *ent*-Kauranoid Diterpenoid from *Hicriopteris glauca* (Gleicheniaceae)

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Abstract: A new *ent*-kauranoid diterpenoid, *ent*-2- -hydroxyl-16-ene-kauran-19-oic acid (1), was isolated from the acetone extract of *Hicriopteris glauca* together with 9 known compounds. Their structures were elucidated by comprehensive NMR and MS analysis.

Key words: Fern; *Hicriopteris glauca*; *ent*-kauranoid diterpenoid; *ent*-2- -hydroxyl-16-ene-kauran-19-oic acid

Hicriopteris glauca (Thunb.) Ching, which belongs to family Gleicheniaceae, is widely distributed in the south of China (Luo *et al.*, 1959). The rhizome of this plant has been used to treat fracture and stomach-ache in Chinese folk medicine (Wu *et al.*, 2006). To the best of our knowledge, only one metabolite (ponasterone A) has been reported from this plant up to now (Takemoto *et al.*, 1973). As a part of our systematic phytochemical studies on metabolites from the fern plants (Li *et al.*, 2006; 2007), the chemical constituents

of *H. glauca* were investigated and a new *ent*-kauranoid diterpenoid, *ent*-2- -hydroxyl-16-ene-kauran-19-oic acid (1), was isolated together with 9 known compounds, 19-hydroxyl-17-nor-16-ene-kauranone (2) (Vieira *et al.*, 2002), *ent*-16, 17, 19-trihydroxyl-kaurane (3), (Tadayuki *et al.*, 1983), *ent*-16, 17-dihydroxyl-kauran-19-oic acid (4) (Kazuo *et al.*, 1976), *ent*-16, 17-dihydroxyl-kauran-19-oic acid (5) (Wu *et al.*, 1996), (6*S*, 13*S*)-cleroda-3, 14-diene-6, 13-diol (6) (Tadashi *et al.*, 1997), trans-4-

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p-hydroxyphenylbut-3-en-2-one (7) (Toshiya *et al.*, 1991), *p*-Coumaric acid (8) (Ann and Kelvin, 1978), Aesculetin (9) (Cussans and Huckerby, 1975), and apigenin (10) (Shen *et al.*, 1993). Reported herein, was the isolation and structural elucidation of the new diterpenoid from *H. glauca* (Thunb.) Ching (Fig. 1).

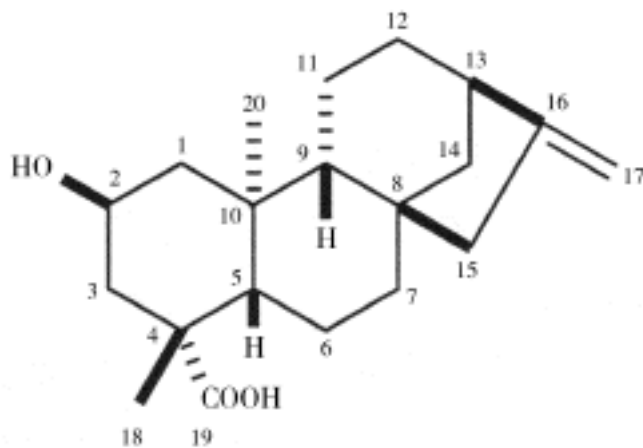


Fig. 1 Structure of compound 1

Results and Discussion

Compound 1 was obtained as colorless powder; its molecular formula was determined to be C₂₀H₃₀O₃ by negative HR-ESI-MS ([M-H]⁻ 317.2116, calcd. 317.2116) and ¹³C NMR spectrum, which indicated six degrees of unsaturation. The IR spectrum showed absorption of hydroxyl group bands (3426 cm⁻¹), carbonyl group (1696 cm⁻¹), and double bond (1657 cm⁻¹). The ¹H and ¹³C NMR spectra (Table 1) of 1 showed 20 carbon resonances due to one carboxylic acid group (δ_C 181.2), one terminal double bond (δ_C 156.0, 103.8; δ_H 4.75 and 4.79, s, each 1H), 3 quaternary sp³ carbons, 4 methines (including an oxygenated one), 8 methylenes, and 2 methyls. Considering the characteristic quaternary carbons at δ_C 45.3, 45.8, and 42.1 ascribable for C-4, C-8, and C-10, three typical methines at δ_C 57.6, 56.4, and 45.2 for C-5, C-9, and C-13, two methyls at δ_C 29.4 and 17.4 for C-18 and 20, together with the characteristic terminal double bond, compound 1 can be ascribed to be a typical kauranoid diterpenoid (Enriquez *et al.*, 1996; Herz *et al.*, 1983; Ohno *et al.*, 1979).

The ¹H and ¹³C NMR data (Table 1) of 1 is very similar to those of kaur-16-*en*-19-oic acid, an *ent*-kauranoid diterpenoid previously isolated from various spe-

cies of *Helianthus* (Herz *et al.*, 1983; Ohno *et al.*, 1979). The only difference observed in the ¹H and ¹³C NMR spectra was the presence of one oxymethine (δ_C 65.0; δ_H 4.08, m) in 1 instead of the methylene carbon at δ_C 19.2 in kaur-16-*en*-19-oic acid. In addition, the chemical shift value of C-1 and C-3 was also downshift from δ_C 40.8 and 37.8 in kaur-16-*en*-19-oic acid to δ_C 50.7 and 48.5 in 1, respectively. Therefore, compound 1 was deduced to be the 2-hydroxyl derivative of kaur-16-*en*-19-oic acid, which can be confirmed by the ¹H-¹H COSY correlations of H-2 with H-1 and H-3 together with the HMBC correlations of H-2 C-1, H-1 C-2, H-2 C-3, H-3 C-2, H-2 C-4, and H-2 C-10. In addition, the fragments obtained by the ¹H-¹H COSY experiment, H-1 H-2 H-3, H-5 H-6 H-7, and H-9 H-11 H-12 H-13, together with the HMBC correlations from H-20 to C-1, C-5, C-9, and C-10, from H-18 to C-3, C-4, and C-5, from H-17 to C-13, C-15, and C-16, and from H-9 to C-8 and C-10 confirmed the structure of compound 1 furthermore.

The relative stereochemistry of 1 was determined on the basis of ROESY experiment to be the same with kaur-16-*en*-19-oic acid. The obvious NOE correlations of H-9 H-1, H-9 H-15, H-5 H-1, H-15 H-12, and H-5 H-18 indicated that these protons were all α -oriented. In the same spectrum, the correlations between H-3 and H-2, H-2 and Me-20, H-14 and Me-20, and between H-1 and H-11 also suggested the α -orientation of the H-2, and Me-20.

Table 1 ¹³C and ¹H NMR data (CD₃OD, in ppm, J in Hz) for 1

No.	¹³ C	¹ H	No.	¹³ C	¹ H
1	50.7 t	2.19 (m)	11	19.6 t	1.65 (m)
1		0.69 (t, 11.3)	12	34.1 t	1.64 (m)
2	65.0 d	4.08 (m)	12		1.47 (m)
3	48.5 d	2.39 (m)	13	45.2 d	2.61 (m)
3		0.93 (t, 11.3)	14	40.8 t	1.98 (m)
4	45.3 s		14		1.12 (m)
5	57.6 d	1.04 (m)	15	50.1 t	2.02 (m)
6	22.8 t	1.83 (m)	16	156.0 s	
7	42.4 t	1.50 (m)	17	103.8 t	4.79 (s)
8	45.8 s		18	29.4 q	4.75 (s)
9	56.4 d	1.11 (m)	19	181.2 s	1.12 (3H, s)
10	42.1 s		20	17.4 q	0.98 (3H, s)

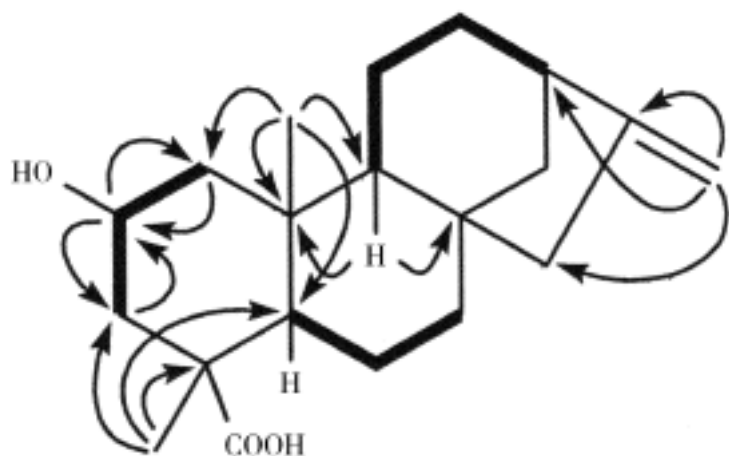


Fig. 2 Key HMBC (—) and COSY (---) correlations of 1

On the basis of all the above evidence, the structure of 1 was established and named as *ent*-2-hydroxy-16-ene-kauran-19-oic acid.

Experimental

General Experimental Procedures Both 1D and 2D NMR experiments were performed on a Bruker AM-400 or on a DRX-500 spectrometer. Chemical shifts (δ) was expressed in ppm with reference to the solvent signals. MS was recorded on a VG Auto Spec-3000 or on a Finnigan MAT 90 instrument. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer for KBr pellets. UV data were obtained on a UV 210A spectrometer. Optical rotations were measured with a Horiba SEPA-300 polarimeter or a Perkin-Elmer model 241 polarimeter. Column chromatography was performed either on silica gel (200–300 mesh, Qingdao Marine Chemical, China), silica gel H (10–40 μm, Qingdao Marine Chemical, China), or MCI gel CHP20P (75–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan). Semi-preparative HPLC was performed on a Hewlett Packard instrument (column: Zorbax SB-C18, 250 × 9.4 mm; UV detector). Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H₂SO₄ in EtOH.

Plant Material The fronds of *Hicriopteris glauca* (Thunb.) Ching were collected from Caiyanghe, Simao town, Yunnan province, P. R. China, in May 2005, and was identified by Prof. Xiao Cheng.

Extraction and Isolation The dry aerial parts of *Hicriopteris glauca* (Thunb.) Ching (20 kg) were powdered and extracted with acetone (3 × 30 L) for 24 hours at room temperature. The acetone extract was concentrated in vacuo to give a crude extract which was then suspended in H₂O and extracted with EtOAc. The organic layer was concentrated in vacuo. The residue (650 g) was then subjected to column chromatography (CC) over silica gel (200–300 mesh) eluted with petroleum ether-acetone (from 1:0 to 0:1) to give fractions A–E. Fraction B was subject-

ed to silica gel chromatography eluted with Petroleum ether *i*-PrOH (10:1) to obtain four fractions (B₁–B₄). Fraction B₁ was purified by silica gel CC using CHCl₃:EtOAc (10:1) to yield compounds 2 (12 mg) and 6 (70 mg). Fraction B₂ was separated on Sephadex LH-20 eluted with CHCl₃:MeOH (1:1), and the further purified by semi preparative HPLC (MeOH:H₂O, 82:18, 3 ml/min) gave 1 (50 mg) and 4 (27 mg). Fraction B₃ was subjected to silica gel eluted with CHCl₃:*i*-PrOH (10:1) to yield 3 (17 mg). Fraction B₄ was chromatographed over a column of Rp C-18 silica gel eluted with MeOH:H₂O (80:20) to give 5 (6 mg). Fraction C was subjected to Sephadex LH-20 eluted with CHCl₃:MeOH (1:1) to yield compounds 8 (31 mg) and 10 (25 mg), further purified by Rp C-18 with MeOH:H₂O (70:30) to give 7 (14 mg) and 9 (19 mg).

Known components were fully characterized by comparison of the ¹H and ¹³C NMR data with those reported in the literature.

Compound 1: colorless powder; [α]_D²² = -65.6 (c = 1.5, CHCl₃); IR (KBr) _{max} 3426, 2929, 2854, 1696, 1657, 1470, 1448 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1; negative FAB/MS: *m/z* 317 [M-H]⁻; HRFAB-MS *m/z* 317.2116 (calcd. for C₂₀H₂₉O₃ 317.2116).

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